Cationic Imido Alkylidene Complexes of Molybdenum Supported by *β*-Diketonate and *β*-Diketiminate Ligands

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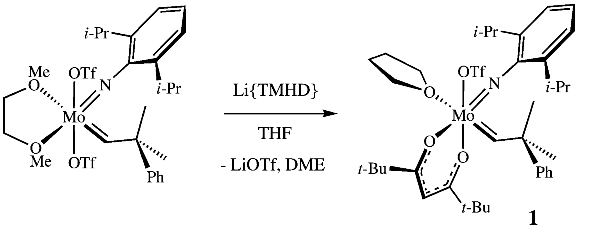
Summary: Reaction of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (Ar = 2,6-i-Pr$_2$C$_6$H$_3$) with the lithium salt of various β-diketonates and β-diketiminates leads to complexes of the type Mo(NAr)(CHCMe$_2$Ph)(L)(OTf) (L = β-diketonate or β-diketiminate). Treatment of these compounds with NaB[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$ in dichloromethane affords rare examples of cationic imido alkylidene complexes. The solid-state structures of two of these compounds, {Mo(NAr)(CHCMe$_2$Ph)(TMHD)(THF)}{B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$} and {Mo(NAr)(CHCMe$_2$Ph)(Ar^{Cl}-Nacnac)}{B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$} (TMHD = tetramethylheptanedionato, Ar^{Cl}-Nacnac = [2,6-Cl$_2$C$_6$H$_3$NC(Me)]$_2$CH), have been determined by X-ray diffraction, and their reactivity with ethylene and other simple olefins has been explored.

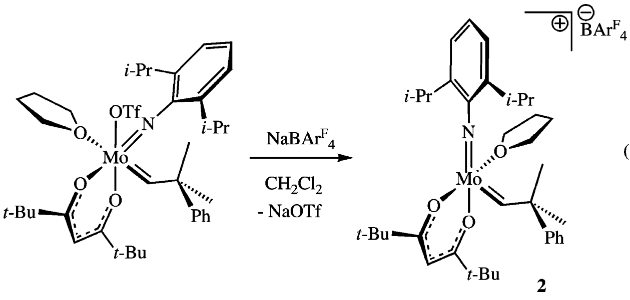
Olefin metathesis has become a powerful tool for the synthesis of new organic molecules and polymers.[1] The most well-developed catalysts that are capable of effecting this transformation are molybdenum or ruthenium alkylidene compounds. Molybdenum compounds usually contain a bulky alkylidene (initially, e.g., neopentylidene), a bulky imido group (e.g., 2,6-diisopropylphenyl), and two bulky alkoxides (e.g., hexafluoro-*tert*-butoxide).[2] We sought to prepare cationic Mo alkylidene complexes in order to study the effect of modification of the traditional catalyst framework. High oxidation state cationic olefin metathesis catalysts of tungsten[3] and molybdenum[4] are rare, especially those that do not contain a coordinating anion. There are several reports of catalytically active cationic ruthenium alkylidenes.[5]

To produce cationic alkylidene compounds that resemble Mo bis-alkoxide catalysts, we first explored *β*-diketonates. Reaction of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) with Li{TMHD} (TMHD = 2,2,6,6-tetramethylheptane-3,5-dionato) in the presence of THF produced Mo(NAr)(CHCMe$_2$Ph)(TMHD)(OTf)(THF) (**1**) in good yield (eq 1). Compound **1** exists as the *syn* isomer, as shown through NMR studies and X-ray crystallography.[6] It is soluble in organic solvents and may be crystallized conveniently from pentane. If THF is absent from the reaction, a base-free species (as judged by ^{1}H NMR) can be isolated, although the yield is lower. The base-free species is less soluble than the THF adduct perhaps as a consequence of formation of an oligomeric structure.



(1)

Treatment of **1** with Na{BAr$^F_4$} (BAr$^F_4$ = B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$) in methylene chloride affords the soluble cationic complex {Mo(NAr)(CHCMe$_2$Ph)(TMHD)(THF)}{BAr$^F_4$} (**2**) and insoluble NaOTf (eq 2). Compound **2** is a yellow crystalline solid that is soluble in THF and halogenated solvents. NMR spectra (in CD$_2$Cl$_2$) of material crystallized from a mixture of dichloromethane and pentane show one isomer with an alkylidene H$_\alpha$ resonance at 13.02 ppm and a C$_\alpha$ resonance at 323.3 ppm. The $^1J_{CH}$ value of 125 Hz is consistent with the formulation of **2** as a *syn* alkylidene.[7,2a]



(2)

Crystals of **2** suitable for X-ray diffraction were grown by diffusion of pentane into a saturated CH$_2$Cl$_2$ solution at −25 °C. The solid-state structure of the cation is shown in Figure 1. The geometry of the complex is best described as a square pyramid with the alkylidene group occupying the apical position. The mean deviation of the Mo atom out of the plane formed by the four basal atoms (O1, O2, O1T, and N1) is 0.3 Å. The Mo−C1 and Mo−N1 distances are within the range typically encountered for four-coordinate alkylidene compounds possessing two alkoxide ligands.[2a,7b] No close contacts were found

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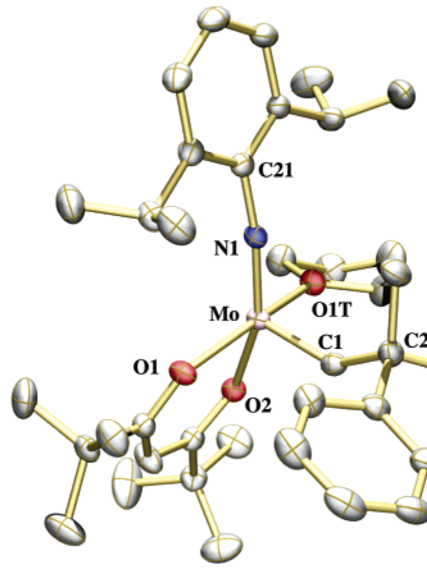
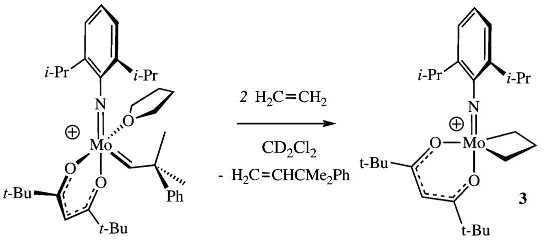


Figure 1. POV-ray rendering (ellipsoids at 50%) of the cation of **2**. Hydrogen atoms, solvent molecules, and the anion are not shown. Selected bond distances (Å) and angles (deg): Mo−C1 = 1.893(3); Mo−N1 = 1.745(2); Mo−O1 = 2.0677(18); Mo−O2 = 2.0540(18); Mo−O1T = 2.1385(18); N(1)−Mo−C(1) = 101.07(10); Mo−C(1)−C(2) = 142.4(2); Mo−N(1)−C(21) = 167.89(18); O(1T)-Mo−O(2) = 158.79(8); N(1)−Mo-O(1) = 156.49(9).

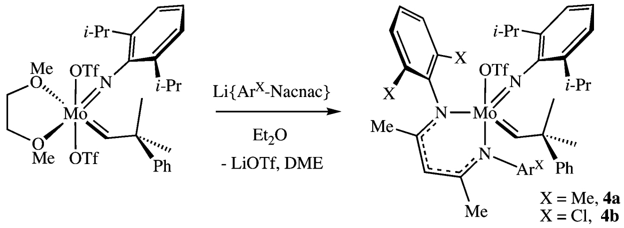
between the cation and either the anion or the cocrystallized solvent molecules.

Reaction of **2** with diallyl ether and norbornene resulted in consumption of the original alkylidene, as judged by ^1H NMR, but did not lead to the products of ring-closing metathesis (RCM) or ring-opening metathesis polymerization (ROMP), respectively. The lack of productive metathesis of these olefins led us to examine the reaction of **2** with ethylene. Exposure of a CD_2Cl_2 solution of **2** to 1 atm of ethylene at room temperature yielded several new species, one of which we propose to be a cationic unsubstituted metallacycle complex (**3**; eq 3) on the basis of multiplets at 5.75 and 5.43 ppm for the α protons and 0.41 and 0.29 ppm for the β protons in its ^1H NMR spectrum. (The ratio of α to β protons is 2:1.) Similar reactions with $^{13}C_2H_4$ show a doublet resonance at 108.51 ppm (J_{CC} = 11.5 Hz) and a triplet resonance at −3.51 ppm (J_{CC} = 11.5 Hz), consistent with a metallacyclobutane complex.[7b,8a] Resonances for the initial metathesis product, 3-phenyl-3-methylbutene, are present, along with a singlet resonance at 0.24 ppm (J_{CH} = 155 Hz), which we attribute to cyclopropane. In experiments involving $^{13}CH_2{=}^{13}CH_2$ the singlet resonance for the cyclopropane carbon atoms was observed at −2.90 ppm. A smaller singlet resonance is also observable in the ^{13}C NMR spectrum at −3.11 ppm that we attribute to *cyclo*-$PhCMe_2C_3H_5$ derived from the initial metallacyclobutane. Traces of propylene (<5%) are also observed in the ^{13}C NMR spectra. The most interesting finding is the formation of cyclopropanes, which typically are generated only as minor products, if at all, in reactions of Mo imido alkylidene complexes with ethylene.[8] Destruction of alkylidene complexes through formation of cyclopropanes could explain the lack of significant catalytic activity in the metathesis reactions noted above. However, the fact that **3** is observable and apparently does not lose cyclopropane in the presence of ethylene begs the question as to how cyclopropanes are formed and why metathesis activity is not observed. So far we have not been able to isolate **3**.



3 (3)

We turned our attention to the more electron-rich and sterically demanding β-diketiminates.[9] As with the β-diketonates, treatment of $Mo(NAr)(CHCMe_2Ph)(OTf)_2(DME)$ with Li{Ar^X-Nacnac} (Ar^X-Nacnac = $[2,6\text{-}X_2C_6H_3NC(Me)]_2CH$, X = Me, **4a**; Cl, **4b**) afforded the analogous triflate complexes shown in eq 4. Unlike **1**, the β-diketiminate complexes do not bind THF. Compounds **4a** and **4b** can be isolated in moderate to good yield. Both **4a** and **4b** are soluble in ethers and aromatic solvents, but are insoluble in pentane. NMR spectra of **4a** show predominantly the presence of the *syn* isomer in solution (98%), but spectra of **4b** indicate it to be a 5:1 mixture of *syn* and *anti* isomers. The *syn* alkylidene resonance for **4b** in C_6D_6 appears at 12.87 ppm compared to 11.56 ppm for **4a**. Treatment of **4a** with $NaBAr^F_4$ in CD_2Cl_2 did not lead to clean formation of a cationic alkylidene complex (according to NMR spectra), although NaOTf formed and precipitated from solution. In contrast, treatment of **4b** with $NaBAr^F_4$ in CH_2Cl_2 afforded {$Mo(NAr)(CHCMe_2Ph)(Ar^{Cl}$-Nacnac)}{$BAr^F_4$} (**5**) cleanly in satisfactory yield (eq 5). The presence of a fifth (donor) ligand appears necessary to stabilize the cationic complexes toward decomposition (as with THF in complex **2**), a requirement that in this case can be fulfilled through intramolecular coordination of the ortho chloride, as shown in an X-ray study (*vide infra*). Compound **5** is an orange-yellow crystalline solid that is soluble in ethers and halogenated solvents. NMR spectra (CD_2Cl_2) of **5** are consistent with it being one major isomer (91%) in solution with an H_α resonance at 13.10 ppm and a C_α resonance at 320.0 ppm. The J_{CH} value of 116 Hz for the major isomer is consistent with its formulation as a *syn* species. Two minor isomers are also apparent with H_α resonances at 15.15 (5.4%) and 14.91 (3.6%) ppm. The minor isomers are believed to be *anti*



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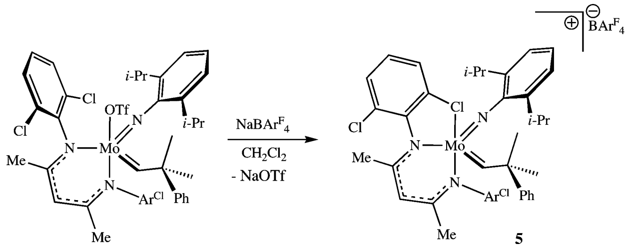

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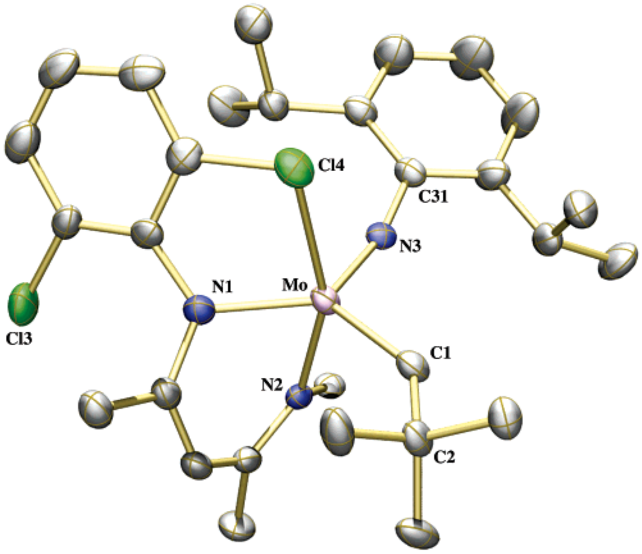

Figure 2. POV-ray rendering (thermal ellipsoids at 50%) of the cation of **5**. Hydrogen atoms, solvent molecules, the anion, the phenyl group of the neophylidene, and the dichlorophenyl substituent bound to N2 are not shown for clarity. Selected bond distances (Å) and angles (deg): Mo−C1 = 1.925(18); Mo−N3 = 1.732(7); Mo−N1 = 2.109(3); Mo−N2 = 2.066(3); Mo−Cl4 = 2.581(5); N3−Mo−C1 = 102.1(10); N1−Mo1−N2 = 84.47(11); Mo1−C1−C2 = 135.3(1), Mo1−N3−C31 = 166.2(15); Cl4−Mo−N1 = 164.3(3).

alkylidenes with relatively strong Mo−Cl interactions. (Bases have been shown to bind more strongly to *anti* alkylidenes.[2a,7a])

The solution NMR spectrum of the major isomer of **5** at 20 °C in CD$_2$Cl$_2$ displays single resonances for both the neophylidene methyl groups and the isopropyl groups of the aryl imido; the structure in solution has a mirror plane of symmetry and a freely rotating 2,6-diisopropylphenyl ring on the NMR time scale. At −90 °C (see Supporting Information, Figure S1) the NMR spectrum of **5** is consistent with the structure depicted in eq 5, with no rotation of the 2,6-diisopropylphenyl ring about the N−C$_{ipso}$ axis. Therefore if a donor chloride to metal bond persists in solution, it must be too weak to maintain the structure shown in eq 5 on the NMR time scale at room temperature. Intramolecular weak coordination of a chloride is an interesting way to create higher coordinate compounds that are more stable to intermolecular reactions, yet react readily upon dissociation of the chloride from the metal.

Diffusion of pentane into a saturated CH$_2$Cl$_2$ solution afforded crystals of **5** suitable for X-ray diffraction. The solid-state structure of the cation of **5** is shown in Figure 2. The geometry is best described as a trigonal bipyramid with Cl4 and one of the Nacnac nitrogen atoms (N2) occupying the axial positions. Unlike **2**, the structure of **5** is similar to the structures of various base adducts of four-coordinate alkylidene species with the alkylidene and imido groups residing in the equatorial plane.[2a] Interestingly, cation **5** exists solely as the *anti* isomer in the solid-state structure. We do not know whether the bulk crystalline form consists entirely of the *anti* isomer or whether we chose a crystal of an *anti* isomer for the X-ray experiment. The Mo−C1 distance of 1.925(18) Å in **5** is slightly longer than in **2**, but in the range encountered for generally longer *anti* Mo═C bonds in Mo(VI) alkylidene species.[2a,7b] The Mo−Cl4 contact of 2.581(5) Å is consistent with a dative interaction.

The reactivity of **5** with several different olefins in CD$_2$Cl$_2$ was examined. Unlike **2**, compound **5** will polymerize 44 equiv of norbornene at room temperature to give a 75:25 mixture of *cis* to *trans* polynorbornene. Little of the initial **5** is consumed in the process, consistent with rapid propagation relative to initiation. Reaction of **5** with 44 equiv of diallyl ether did not afford dihydrofuran in 24 h at room temperature; we believe that coordination of the ether functionality to the electrophilic metal center is responsible for a lack of productive metathesis of diallyl ether. Compound **5** was found to react with allyltrimethylsilane and diallyldimethylsilane to give a new alkylidene, with triplet H$_\alpha$ resonances at 13.57 and 14.42 ppm, respectively. Exposure of 1 atm of propylene to a solution of **5** in CD$_2$Cl$_2$ yielded a mixture of *cis* and *trans* 2-butene, ethylene, and propylene. These results suggest that complex **5** is a metathesis initiator, although at this time we do not know how long-lived various alkylidenes are in various reactions and what the processes are that lead to catalyst decomposition and loss of activity.

In conclusion, we have prepared the first cationic versions of Mo imido alkylidene catalysts that contain a weakly coordinating anion and have explored their initial metathesis reactivity. Synthesis of compounds that contain other Nacnac ligands and imido groups is currently underway. We suspect that there will be some fundamental differences in reactions that involve cationic species compared to the neutral bis-alkoxide catalysts.

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Supporting Information Available: Complete experimental details for all compounds, VT NMR spectrum of **5**, and thermal ellipsoid diagrams and crystallographic information files for **2** and **5**. Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Data for the X-ray structure is also available to the public at http://www.reciprocalnet.org/ (**2** = 05220; **5** = 06070).

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